Nanoimprint Technology for Fabrication of Transducers – Redox Reactions at the Nanoscale

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Next generation lithographies (NGL) emerged in the early 90's as the cost for development of UV-lithography increased dramatically. Nanoimprint has developed to the level where it can be used as a tool for making nanometer structures. This cost-efficient, high throughput method opens new doors for interdisciplinary nanoscale research and the commercialization of it. Obvious applications are sensors and especially nanometer structured transducers for use in pharmaceutical, medical or (bio-) chemical analysis, which have so far not been accessible on a large scale.

Many of the challenges put forth in this area can be addressed by nanoimprint lithography (NIL). Here, we introduce a method on how to fabricate nanometer structured interdigitated array electrodes (IDA) including interconnections and bondpads, in the micrometer range, in a single imprint step on 2-inch wafer scale. The method enables mass production of the devices at low cost, initiating a new field for the commercial use of nanometer structured sensor systems.

The basic design of the IDA can be used as transducer in many different fields. Typical applications are highly sensitive capacitive sensors [1], surface acoustic wave resonators [2], and slightly modified as MEMS, in accelerometers, e.g. for air bags [3]. In our case we use the IDA's for an electrochemical purpose. Theoretical work in this area has been performed by Aoki et al. [4,5,6]. When reducing the spacing between the electrode fingers down to a couple of micrometers or below an electrochemical effect known as redox cycling can be observed when applying potentials e.g. 100 mV above and below the formal potential of a redox couple to each half electrode of the IDA. When the electrode distance approaches the diffusion layer thickness one can observe current amplification through continuous cycling of a redox species between the two finger electrodes. The effect increases with decreasing electrode distance making it possible to build new, highly sensitive electrochemical sensors by manufacturing those electrodes in the nm-range [7].

Following theoretical calculations the current amplification, should increase with decreasing electrode spacing. We investigated this effect by using electrodes spanning two orders of magnitude, from 15 m to 100nm, figure 1 shows the current density as a function of electrode distance normalized over area. It is clear from this that one can make highly sensitive electrochemical sensors by manufacturing electrodes in the nanometer range. However, in order to be able to manufacture the IDA's by nanoimprint, process development in several different areas has been necessary.

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The stamp is made on a 2" silicon wafer with 350nm of SiO_2 on top. To define the Cr metal etch mask a combination of UV-lithography, for the larger structures, and EBL, for smaller ones, is needed [8,9]. CHF_3 based reactive ion etching (RIE), is employed to etch the SiO_2, for a final stamp profile height of 100nm. Before the stamp can be used it is treated with an anti-adhesion layer. This is done by CVD of tridecaflouro-(1H, 1H, 2H, 2H) tetrahydrooctyl trichlorosilane in a nitrogen atmosphere [10].

By including contact pads on the stamp, a mix and match process can be avoided in the lithography step. However, imprinting large structures, i.e. $>50\,\mu m^2$ with 100% pattern density, is problematic. The stamp may buckle and give rise to ellipsoidal resist profile. To solve this problem we include cavities to accommodate the displaced polymer. This creates the cross-hatched looking contact pads shown in figure 2 and enables us to combine large and small structures in a one step imprint lift-off process.

The imprinting is done on an Obducat machine using 2" silicon wafers with 850nm of insulating SiO_2 on top. For an efficient lift-off process we use a bilayer resist scheme with PMMA on LOL2000 [11]. The imprint parameters are; temperature 220°C, pressure 50bar and hold time 5min. After separation we use oxygen ashing to remove residual PMMA. An undercut profile is created when the LOL is dissolved in MF319. Metal evaporation is done and finally we use aceton and remover 1165 for lift-off.

The metal of choice for the electrodes is Au, this requires an adhesion promoter, usually Cr or Ti. However, in electrochemical applications these metals will act as galvanic elements and corrode. An alternative is mercaptopropyl trimethoxysilane (MPTS) which bonds covalently to both silicon atoms and gold. The molecule is applied by CVD onto the imprint wafer before the polymers are deposited [12].

Measurements on imprinted structures, with 800nm line and spacing and show linear behavior with concentration (figure 3a) and fast response time (figure 3b). Both effects are predicted by theory.

In conclusion we have shown there is motivation for miniaturizing interdigitated array electrodes for electrochemical applications such as redox cycling. We have developed processes for stamp manufacturing and lift-off for nanoimprint lithography. These have been successfully applied to IDA's. An alternative solution to adhesion problems of gold on silicon has been suggested. Finally sample IDA chips have been measured yielding results coinciding with theory.

[1] P. van Gerwen, W. Laureyn, W. Laureys, G. Huyberechts, M. op de Beeck, K. Baert, J. Suls, W. Sansen, P. Jacobs, L. Hermans, R. Mertens: Nanoscaled Interdigitated Electrode Arrays for Biochemical Sensors, Sensors and Actuators B, 49, (1998), pp.73-80.
[2] E. Benes, M. Gröschl, W. Burger, M. Schmid: Sensors based on piezoelectric resonators, Sensors and Actuators A, 48 (1995) pp.1-21.
[3] O. Lüdtke, V. Biefeld, A. Buhrdorf, J. Binder: Laterally driven accelerometer fabricated in single crystalline silicon, Sensors and Actuators, 82 (2000) pp.149–154.
[4] K. Aoki, M. Morita, O. Niwa, and H. Tabei: Quantitative analysis of reversible diffusion-controlled currents of redox soluble species at interdigitated array electrodes under steady-state conditions, Journal of Electroanalytical Chemistry, 256, (1988), pp.269-282.
[5] K. Aoki and M. Tanaka: Time-dependence of diffusion-controlled currents of a soluble redox couple at interdigitated microarray electrodes, Journal of Electroanalytical Chemistry, 266, (1988), pp.11-20.

[6] K. Aoki, K. Tokuda and H. Matsuda: Derivation of an Approximate Equation for Chronoamperometric Curves at Microband Electrodes and its Experimental Verification, Journal of Electroanalytical Chemistry, 230, (1987), pp.61-67.
[7] Y. Iwasaki, M. Morita: Electrochemical Measurements with Interdigitated Array Electrodes, Current Separations, 14(1), (1995), pp.2-8.
[8] I. Maximov, E.-L. Sarwe, M. Beck, K. Deppert, M. Graczyk, M.H. Magnusson, L. Montelius: Fabrication of Si-based nanoimprint stamps with sub-20 nm features, Microelectronic Engineering, 61–62, (2002), pp. 449–454.
[9] M. Beck, P. Carlberg, F. Persson, M Graczyk, I. Maximov, T.G.I. Ling, L. Montelius Nanoelectrochemical transducers for (bio-) chemical sensor applications fabricated by nanoimprint lithography Submitted
[10] M. Beck, M. Graczyk, I. Maximov, E.-L. Sarwe, T.G.I. Ling, L. Montelius, M. Keil: Improving stamps for 10 nm level wafer scale nanoimprint lithography, Microelectronic Engineering, 61-62, (2002), pp.441-448.
[11] P. Carlberg, M Graczyk, E.-L. Sarwe, I. Maximov, M. Beck, L. Montelius: Lift-off Process for Nanoimprint Lithography, Microelectronic Engineering 67-68 (2003), pp 203-207
[12] T.G.I. Ling, M. Beck, R. Bunk, E. Forsén, J.O. Tegenfeldt, A.A. Zakharov, L. Montelius: Fabrication and characterization of a molecular adhesive layer for micro- and nanofabrication electrochemical electrodes, Microelectronic Engineering 67-68 (2003), pp 887-892

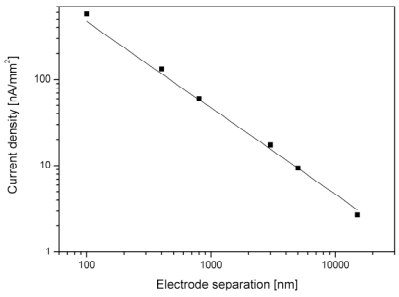

Figure 1. The graf shows current density vs. electrode separation normalize over sensor area. It is clear that the sensitivety of a potential sensor increases radically when the dimensions area decreased. The solid line represents theoretical calculation. 2□m measurement from J.Electroanal.Chem 256(1988) 269-282. 5□m measurement from J.Electroanal.Chem. 266(1989) 11-20.

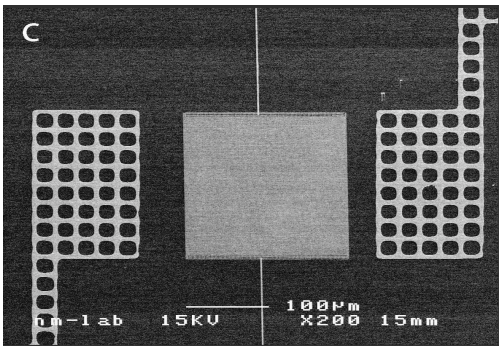

Figure 2. SEM micrograph showing lift-off results of large area structures. A cross hatched structure structure is used to facilitate poly3er flow. Thus avoiding uneven polymer thickness of large and small structures after imprint.

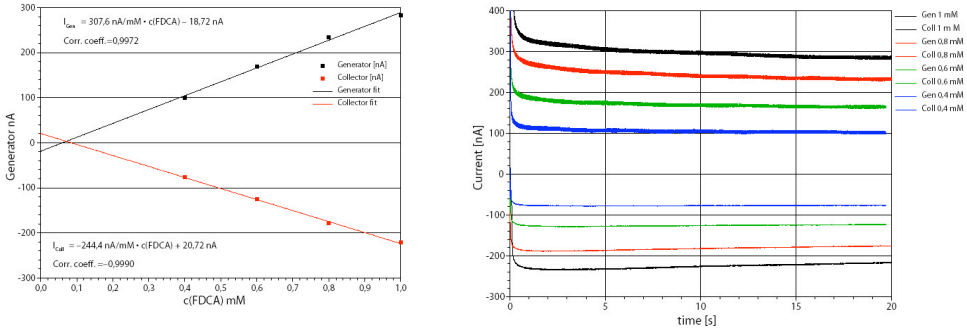

Fig3. Left 3a: Series of redox cycling chronoamperometry measurements in ferrocene dicarboxylic acid of different concentraition. Right 3b: Chronoamperotemetry measurements showing that steady state current is reached after approximately 10s.